(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/18272 A1

(51) International Patent Classification[7]: C01B 31/02

(21) International Application Number: PCT/US01/26269

(22) International Filing Date: 23 August 2001 (23.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/648,860 25 August 2000 (25.08.2000) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/18272 A1

(54) Title: METHOD OF MAKING A CARBON FOAM MATERIAL AND RESULTANT PRODUCT

(57) Abstract: A method of making anisotropic carbon foam material includes deashing and hydrogenating bituminous coal, separating asphaltenes from oils contained in the coke precursor, coking the material to create a carbon foam. In one embodiment of the invention, the carbon foam is subsequently graphitized. The pores within the foam material are preferably generally of equal size. The pore size and carbon foam material density may be controlled by (a) altering the percentage volatiles contained within the asphaltenes to be coked, (b) mixing the asphaltenes with different coking precursors which are isotropic in nature, or (c) modifying the pressure under which coking is effected. In another embodiment of the invention, solvent separation is employed on raw bituminous coal and an isotropic carbon foam is provided. A related carbon foam product is disclosed. The carbon foam materials of the present invention are characterized by having high compressive strength as compared with prior known carbon foam materials. A further embodiment is disclosed wherein a petroleum pitch is employed as the feedstock either alone or in combination with a coal feedstock.

METHOD OF MAKING A CARBON FOAM MATERIAL AND RESULTANT PRODUCT

CROSS REFERENCE TO RELATED APPLICATION

This application is a Continuation-in-Part of United States Patent Application Serial No. 09/095,909, filed June 11, 1998, which is a division of United States Patent Application Serial No. 08/887,556 entitled "Method of Making a Carbon Foam Material and Resultant Product," filed July 3, 1997, now U.S. Patent 5,888,469, which was a continuation of United States Patent Application Serial No. 08/455,742, filed May 31, 1995, abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of making an improved carbon foam material and particularly a graphitized carbon foam material having superior compressive strength and electrical conductivity.

2. Description of the Prior Art

It has been known for many decades that coal can be beneficiated for application in a wide variety of environments. For example, it has been known that coal may be employed as a fuel in electric utility plants and, in respect of such usages, beneficiating of the coal will reduce the ash content and the amount of sulfur and nitrogen species contained in the gaseous exhaust products.

It has also been known to convert coal into coke for use in various process metallurgy environments.

It has also been known to create carbon foam materials from feedstocks other than coal, which can be glassy or vitreous in nature, and are brittle and not very strong. These products which lack compressive strength tend to be very brittle and are not graphitizable. See, generally, Wang, "Reticulated Vitreous Carbon - A New Versatile Electrode Material," Electrochimica Acta, Vol. 26, No. 12, pp. 1721-1726 (1981) and "Reticulated Vitreous Carbon An Exciting New Material," Undated Literature of ERG Energy Research and Generation, Inc. of Oakland, California.

It has been known through the analysis of mechanical properties of carbon fibers that long-range crystallite orientation is achieved by alignment of the precursor molecules during fiber spinning. In "Idealized Ligament Formation in

Geometry in Open-Cell Foams" by Hager et al., 21st Biennial Conference on Carbon, Conf. Proceedings, American Carbon Society, Buffalo, New York, pp. 102-103 (1993), a model analysis regarding interconnected ligament networks to create geometric evaluation of hypothetical ligamentous graphitic foam is disclosed. This model analysis, however, does not indicate that graphite foam was made or how to make the same.

It has been suggested to convert synthetic naphthalenic mesophase pitch into a carbon foam product by employing a blowing/foaming agent to create bubbles in the material, followed by graphitization of the resultant carbonized foams above 2300°C. See "Graphitic Carbon Foams: Processing and Characterizations" by Mehta et al., 21st Biennial Conference on Carbon, Conf. Proceedings, American Carbon Society, Buffalo, New York, pp. 104-105 (1993). It is noted that one of the conclusions stated in this article is that the mechanical properties of the graphitic cellular structure were quite low when compared to model predictions.

It has been known to suggest the use of graphitic ligaments in an oriented structure in modeling related to structural materials. See "Graphitic Foams as Potential Structural Materials," Hall et al., 21st Biennial Conference on Carbon, Conf. Proceedings, American Carbon Society, Buffalo, New York, pp. 100-101 (1993). Graphitic anisotropic foams, when evaluated mathematically in terms of bending and buckling properties, were said to have superior properties when compared with other materials in terms of weight with particular emphasis on plate structures. No discussion of compressive properties is provided.

In "Carbon Aerogels and Xerogels" by Pekala et al., Mat. Res. Soc. Symp. Proc., Vol. 270, pp. 3-14 (1992), there are disclosed a number of methods of generating low- density carbon foams. Particular attention is directed toward producing carbon foams which have both low-density (less than 0.1 g/cc) and small cell size (less than 25 microns). This document focuses upon Sol-gel polymerization which produces organic-based aerogels that can be pyrolyzed into carbon aerogels.

In "Carbon Fiber Applications," by Donnet et al., "Carbon Fibers," Marcel Decker, Inc., pp. 222-261 (1984), mechanical and other physical properties of carbon fibers were evaluated. The benefits and detriments of anisotropic carbon fibers are discussed. On the negative side are the brittleness, low-impact resistance and low-break extension, as well as a very small coefficient of linear expansion. This publication

also discloses the use of carbon fibers in fabric form in order to provide the desired properties in more than one direction. The use of carbon fibers in various matrix materials is also discussed. A wide variety of end use environments, including aerospace, automotive, road and marine transport, sporting goods, aircraft brakes, as well as use in the chemical and nuclear industries and medical uses, such as in prostheses, are disclosed.

It has been known to make carbon fibers by a spinning process at elevated temperatures using precursor materials which may be polyacrylonitrile or mesophase pitch. This mesophase pitch is said to be achieved through conversion of coal-tar or petroleum pitch feedstock into the mesophase state through thermal treatment. This thermal treatment is followed by extrusion in a melt spinning process to form a fiber. The oriented fiber is then thermoset and carbonized. To make a usable product from the resulting fibers, they must be woven into a network, impregnated, coked and graphitized. This involves a multi-step, costly process. See "Melt Spinning Pitch-Based Carbon Fibers" by Edie et al., Carbon, Vol. 27, No. 5, pp. 647-655, Pergamen Press (1989).

U.S. Patent 5,705,139 discloses a method of employing the solvent extraction process of U.S. Patent 4,272,349 as a basis for selecting a particular coal extract of bituminous coal to produce isotropic coke and graphite from solid extracts obtained by non-destructive solvent treatment of coal. These materials are all solid. The patent also acknowledges the existence of petroleum pitch which is said to have certain prior uses in respect of a binder pitch, as well as possible use as a raw material for graphite or other carbon articles, but is said to suffer the same disadvantages as petroleum coke.

U.S. Patent 4,025,689 discloses the use of a carbonaceous substance which may be petroleum coke, pitch coke, graphite, coal, charcoal or carbon black in making a graphitized hollow sphere wherein a foamed polystyrene coated with a carbonaceous powder and binder are heated to volatilize the core in making the porous article.. U.S. Patent 4,289,604 discloses a method for manufacturing isotropic coke from a tar or tar pitch.

There remains, therefore, a very substantial need for an improved method of making carbon foam product which has enhanced compressive strength and is graphitizable and the resultant products.

SUMMARY OF THE INVENTION

The present invention has met the above-described needs. In one preferred method of the present invention, a coke precursor is provided by de-ashing and hydrogenating bituminous coal. The hydrogenated coal is then dissolved in a suitable solvent which facilitates de-ashing of the coal and separation of the asphaltenes from the oil constituent. The asphaltenes are subjected to coking, preferably at a temperature of about 325°C to 500°C for about 10 minutes to 8 hours to devolatilize the precursor asphaltenes. The coking process is preferably effected at a pressure of about 15 to 15,000 psig. The anisotropic carbon foam so created is then cooled. In a preferred practice of the invention, the anisotropic carbon foam so created is subsequently graphitized. As an alternate to employing hydrogenation, solvent de-ashing of the raw coal alone may be employed in order to create the asphaltenes which are then coked and graphitized in the same manner. With this approach, an isotropic product is produced from the solvent extraction of raw unhydrogenated coal.

In a preferred practice of the invention, a blend of hydrogenated and unhydrogenated solvent separated asphaltenes may be employed in order to adjust the degree of anisotropy present in the carbon foam. Also, it is preferred that the voids in the foam may be generally of equal size. The size of the individual bubbles or voids may be adjusted by altering the amount of volatile material contained in the asphaltenes or varying the pressure under which coking is effected.

In a preferred practice of the invention, after coking, the foamed material is subjected to calcining at a temperature substantially higher than the coking temperature to remove residual volatile material. The preferred temperature is about 975°C to 1025°C and the time is that which is adequate to achieve a uniform body temperature for the material.

In another embodiment of the present invention, petroleum feedstock is employed to make a carbon foam with anisotropic domains of the present invention. In a variation of this embodiment, the petroleum feedstock may be mixed with coal feedstock to make carbon foams with either isotropic domains or anisotropic domains or

both. In either event, the methods of achieving isotropic and anisotropic carbon foam and custom blended properties as disclosed herein are applicable.

The method produces a graphitized carbon foam product having a compressive strength in excess of about 600 lb/in^2.

It is an object of the present invention to provide a method of producing coal-derived carbon foam which may be graphitized.

It is a further object of the present invention to provide such a method and the resulting product which may be produced by hydrogenating bituminous coal followed by separation of asphaltenes, and coking the same.

It is a further object of the present invention to provide a method and resultant product which permits control of the degree of anisotropy of the carbon foam.

It is a further object of the present invention to provide such a method wherein solvent partitioning of the unhydrogenated coal or hydrogenated coal is employed to select the proper fraction for making the desired foam or removing inorganic species from the coal.

It is a further object of the present invention to provide such a method which permits control over the size of the voids in the carbon foam and the density of the same.

It is a further object of the invention to provide a method of producing such a product which is capable of being graphitized and has much higher compressive strength than previously known carbon foams.

It is a further object of the present invention to provide such a method which produces a controllable, low-density carbon foam product having either isotropic or anisotropic graphite structure which may have open-cell or close-cell configurations.

It is a further object of the present invention to provide a method of producing such a product which is lightweight and possesses a controllable degree of electrical and thermal conductivity.

It is a further object of the present invention to produce a carbon foam product from petroleum feedstock employed alone or employed in a blend with coal feedstock.

It is a further object of the present invention to employ petroleum feedstock in making a carbon foam without requiring the creation of mesophase pitch.

It is yet another object of the present invention to employ in the petroleum feedstock embodiment of the invention a petroleum feedstock which has a high softening point.

These and other objects of the invention will be more fully understood from the following detailed description of the invention on reference to the illustrations appended hereto.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a first embodiment of the method of producing anisotropic graphitized carbon foam of the present invention.

Figure 2 is a second embodiment of a method of producing isotropic graphitized carbon foam of the present invention.

Figure 3 is a schematic diagram of a preferred method of controlling the degree of anisotropy.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As employed herein, the terms "petroleum feedstock" or "petroleum pitch" means a fraction having a softening point of greater than about 100°C resulting from cracking of crude petroleum and can form a Bingham fluid by thermal processing. These terms shall expressly exclude mesophase pitch.

As employed herein, the term "pitch material" shall mean a pitch material which is a coal based pitch or a petroleum pitch or a pitch which is a combination of the two.

As employed herein, the term "pitch precursor" means a carbon containing material which can be converted into a pitch material.

In a preferred practice of the present invention, bituminous coal is provided in size of about -60 to -200 mesh and, preferably, about -60 to -80 mesh. In the embodiment, as shown in Figure 1, wherein anisotropic carbon foam will be produced, the coal is first hydrogenated in step 2. This may be accomplished at a temperature of about 325°C to 450°C at a hydrogen over-pressure of about 500 to 2,500 psig hydrogen cold for a reaction time of about 15 minutes to 1.5 hours. Tetralin may be employed as a proton-donating agent. After the reactor has cooled, the contents are removed and the tetralin separated by distillation. The resulting hydrogenated coal may be exhaustively

extracted with Tetrahydrofuran (THF) with the residue being filtered to remove inorganic matter. It has been found that under these hydrogenating conditions, more than one-half of the coal mass will be rendered soluble in THF. The hydrogenated coal is subjected to preliminary beneficiation as by de-ashing, which may be accomplished in the manner disclosed in Stiller et al., U.S. Patent 4,272,356. The THF portion will contain all of the asphaltenes, or coal-derived pitch precursors, and oils. The THF, after extraction is complete, may be evaporated for recycling and the recovered coal-derived pitch precursor separated by employing a suitable solvent, such as toluene. The toluene-soluble fraction will be referred to generally as "oils" and the remainder referred to as the asphaltene fraction or coal-derived pitch precursor fraction which is dried. This solvent separation step is identified as step 10 in Figure 1.

The next step 12 in creating anisotropic carbon foam is to coke the asphaltenes. Coking is preferably achieved at a temperature of about 325°C to 500°C for a period of about 10 minutes to 8 hours and, preferably, about 15 minutes to 5 hours in an inert gas atmosphere, such as nitrogen or argon gas in a range of about 15 to 15,000 psig (hot) and preferably about 50 to 1000 psig (hot). The pressure is maintained at a generally constant level by means of ballast tank 16.

In a preferred practice of the invention, heating of the oven begins at 350°C and the temperature is raised at a rate of 2°C per minute until the temperature reaches 450°C at which temperature is held for about 5 to 8 hours. After heating, the oven is turned off and the contents are allowed to cool to room temperature slowly, generally over a 5 to 8 hour period. This foaming operation, when conducted in the coking oven in this manner, serves to partially devolatilize the asphaltenes with the evolution of the volatile matter serving to provide bubbles or voids and thereby create the carbon foam product.

If desired, the carbon foam may be used in this form for many uses, such as structural materials, lightweight automotive composites, impact and energy-absorbing structures and heat insulators, for example.

In a preferred practice of the invention, after coking, the foamed material is subjected to calcining at a temperature substantially higher than the coking temperature to remove residual volatile material. The preferred temperature is about

975°C to 1025°C and the time is that which is adequate to achieve a uniform body temperature for the material.

In a preferred practice of the invention, the carbon foam is subjected to graphitizing (step 14) which is preferably accomplished at a temperature of at least 2600°C. The graphitizing step 14 should be continued for a time period long enough to achieve a uniform temperature of at least 2600°C throughout the entire foam material. The larger the specimen, the longer the time required. A small specimen may require about one hour, for example. In the most preferred practice, the process of graphitizing is accomplished at about 2600°C to 3200°C.

In the embodiment of Figure 1, hydrogenation involves large coal molecules being broken apart thermally with the resultant fragments being capped by hydrogen. This results in formation of smaller aromatic molecules. The hydrogenated coal is subjected to solvent extraction by boiling with a solvent to solubilize most of the organic material in the coal. This permits the separation of the inorganic impurities which are not soluble and, therefore, are removed by simple filtration. A second solvent may be employed to separate the desired asphaltene fraction. Once the solvent is evaporated, the resulting extract is a solid which is free from all inorganic impurities. In lieu of boiling with the second solvent, the oil fraction may be separated by a thermal treatment or distillation.

In order to provide further disclosure regarding this first embodiment, an example will be considered.

Example 1

Raw Pittsburgh #8 Coal was hydrogenated by introduction into an autoclave reactor at 350°C for one hour under 1000 psig (cold) hydrogen using 3:1 (weight) tetralin to coal ratio. After cooling, the hydrogenated coal was removed from the reactor and the tetralin was evaporated. The hydrogenated coal was extracted in THF and the residue was filtered to remove the inorganic species. The THF was evaporated from the filtrate and the resultant extract was dissolved in toluene with the undissolved portion being filtered. The toluene was evaporated to recover the extract. The THF soluble/toluene insoluble (asphaltene portion) extract was placed in a reactor with the nitrogen pressure set at 700 psig in order to effect the foaming operation. The starting temperature was 350°C and the temperature was elevated at 2°C /minute until

450°C was reached. It was held at the temperature for five hours and then calcined at 1000°C, after which, it was cooled slowly. The foam was then removed from the reactor. The foam was then graphitized by introducing it into a furnace at a temperature of 2600°C and a pressure of 0 psig argon wherein it was held for one hour which was the time required to heat the particular specimen to a uniform temperature of 2600°C and, after cooling, was withdrawn. This produced an anisotropic graphitized carbon foam.

In an alternate embodiment of the invention, the method may be practiced essentially as is shown in Figure 1, except for elimination of the hydrogenation step 2. This approach is illustrated in Figure 2 wherein the coal is de-ashed (step 22) in a solvent, such as N-methyl pyrrolidone, for example. There is asphaltene separation (step 30), followed by coking of the asphaltenes to create carbon foam (step 32), under the influence of ballast tank 33, and subsequent graphitizing of the carbon foam (step 34). In effecting the solvent extraction, it is preferred that the solvent-to-bituminous coal ratio be about 3:1 to 10:1 and heating to the solvent boiling point.

Calcining may be effected after foaming and before graphitizing. This calcining may be effected at about 975°C to 1025°C.

The alternate approach of Figure 2 produces an isotropic foam carbon which may be graphitized. The bubble or pore sizes of this embodiment will all be equal and control of size may be effected by controlling the amount of volatiles in the asphaltenes, as well as the externally applied pressure through ballast tank 33.

Referring to Figure 3, the degree of anisotropy may be altered by blending (step 44) the hydrogenated asphaltenes (step 40) from step 10 in Figure 1 with unhydrogenated asphaltenes in a solvent (step 42) from step 30 of Figure 2, the latter of which tends to be isotropic. This produces the desired anisotropic characteristics in the final product. The desired degree of anisotropy may be adjusted in this manner in order to provide the preferred properties for the particular end use contemplated. The solvent is evaporated in step 46 after which the asphaltenes are coked in step 48 to create carbon foam and then the carbon foams are graphitized in step 50. Ballast tank 49 is employed to maintain the pressure at the desired level.

With respect to the bubble or void dimension in the foam, the bubbles will generally be of equal dimension to each other. The bubble dimension may be varied

by altering the volatile content of the asphaltenes obtained through the extraction process.

Also, the bubble dimension and density of the carbon foam can be altered by altering the external pressure applied through a ballast tank 16 which is operatively associated with the coking oven (step 12) (FIG. 1), as well as ballast tanks 33, 49 (FIGS. 2 and 3). The higher the ballast pressure applied externally, the smaller the bubble dimension and the higher the density of the resultant product.

The graphitized foams made by the present invention will have a bulk density of about 0.2 to 2 g/cc and, preferably, be about 0.2 to 0.4 g/cc.

It has been found that the graphitized foam product produced in this manner has a very high compressive strength and generally will be greater than about 600 lb/in^2. The compressive strength is related to bubble size with smaller bubble size increasing compressive strength.

If desired, pitch material may be introduced into the voids which communicate with the exterior of the carbon foam so as to enhance the strength. This pitch may be a standard petroleum-based impregnation pitch. This product may be coked in order to devolatilize and strengthen the inserted pitch material. The pitch filling the voids may be baked and graphitized.

Among the advantageous properties of the present carbon foam are that it is lightweight and can be either a thermal insulator, which is electrically conductive, or an efficient conductor of heat and electricity. The foam can be molded into any desired shape by coking within appropriately shaped molds. This provides numerous potential end uses. It may be used for its compressive strength, electrical properties and thermal properties. The material may be used, for example, in membranes for separation of ions in solution or particulates in gases at high temperature, it can be used in thermal management devices, such as substrates for integrated circuits or aerospace applications. The material may also be employed in filters including high temperature filters. Also, depending upon the end use, the degree of thermal conductivity can be altered. In general, the isotropic domain foam is not a high thermal conductor and the non-graphitized foam is a poor thermal conductor and may be employed as thermal insulators. The foam may also find use in building and structural members, such as a substitute for wood and steel beams. It can also be used as a firebreak in aircraft and

naval structures. Numerous, advantageous automotive uses, such as in pistons, vehicle frames, and other structural members, impact absorption uses, such as impact absorbers for doors, and connecting rods, exist. Further, in view of the strength and lightweight nature of the product, aerospace and airplane uses, such as in wings, brakes, as well as satellite and space station structures involve advantage end uses.

The carbon foam product resulting from the captioned invention may be anisotropic as in the first embodiment (FIG. 1) or isotropic (FIG. 2), or with the degree of anisotropic nature being controlled by the nature of the asphaltene materials mixed (FIG. 3). One means of creating the desired level of anisotropic properties would be to admix a predetermined ratio of a solvent extract from hydrogenated coal with the extract from unhydrogenated coal as in Figure 3, in a solvent, such as N-methyl pyrrolidone (NMP). The resultant coal-derived pitch precursor or asphaltene produced after solvent evaporation is employed in the coking operation. By adjusting the ratio of unhydrogenated to hydrogenated coal-derived pitch precursor products, different levels of anisotropy may be achieved. In general, the carbon foam materials will have a compressive strength greater than 600 lb/in^2. In addition to impregnating the foam material with pitch to fill the voids, if desired, such pitch filled void materials may be baked and graphitized, if desired. An alternate approach, for some uses, would be to cover the foam with a thin skin of carbon fibers or pitch to seal the outer surface. This would result in a lightweight, yet strong, structural member. In uses such as a gas or liquid filter for environmental remediation, for example, it may be desirable to activate the surface area of the material.

While it will be appreciated by those skilled in the art that numerous uses may be made of a material having the blend of desired properties of those of the present invention, among additional uses would be as a catalyst support for high temperature catalysts, in biological materials, such as bone and prosthetic items, as well as in environmental waste remediation as by heavy metal removal, electrostatic precipitators and in nuclear waste containers wherein undesired leaching or degradation of the carbon material would be resisted.

A further embodiment of the present invention involving the use of petroleum feedstocks, such as petroleum pitch, will be considered. The petroleum pitch may be substituted in its entirety in any of the processes disclosed herein in respect of the

method of creating a carbon foam with anisotropic domains as disclosed, for example, in connection with Figure 1 hereof. By combining petroleum pitch with coal feedstock, a carbon foam with isotropic domains as disclosed, for example, in connection with Figure 2 can be made. In addition, petroleum pitch can be blended with both hydrogenated and unhydrogenated asphaltenes in achieving a blend of properties as disclosed, for example, in connection with Figure 3. A suitable petroleum pitch may be purchased commercially and employed in the process. One such pitch material is the product sold under the designation A-240 pitch by Ashland Oil Company. Others are also available.

The separation of asphaltenes from the oils will preferably be effected employing a solvent to petroleum pitch or petroleum pitch plus coal feedstock (depending upon which embodiment is employed) ratio of about 3:1 to 10:1.

In the preferred processing which avoids the need to form a mesophase pitch, the petroleum pitch is heated to a softening temperature which in the case of the Ashland Oil Company A-240 pitch, is about 240°F. The pitch is then coked, preferably by placing it in an enclosed stirred reactor at atmospheric pressure and heated to about 300°C to 500°C and preferably is heated to between about 350°C and 400°C while continuously sparging with nitrogen gas. Heating is effected for about 6 minutes to 24 hours with the preferred time being about 5 to 7 hours. Low molecular weight volatiles evolve from the petroleum pitch and the pitch begins to cross-link and thicken. Depending upon the nature of the pitch, the reactivity to cross-linking may vary.

The rheology of the pitch changes to a more Bingham-like fluid suitable for creating foams through the use of a suitable blowing agent. The pitch is then cooled to room temperature and, if desired, can be crushed into a powder form, preferably less than 30 mesh. The processed petroleum pitch can then be placed in a foaming reactor and made into foam in accordance with any of the methods disclosed herein in respect of the methods employing coal pitch.

The carbon foam may then be calcined at a temperature substantially higher than the coking temperature. Calcining is preferably effected at a temperature of about 975°C to the crystallization temperature and preferably about 975° to 1025°C. The carbon foam may then be graphitized, if desired, preferably at a temperature of at least 2600°C and preferably about 2600°C to 3200°C.

In a refinement of this third embodiment, coal feedstock or pitch, which is preferably bituminous coal extract, may be mixed with petroleum pitch in order to modify the reactivity of the petroleum pitch toward cross-linking in the thermal treatment. The coal employed to form the coal extract may be identical as that described in the other embodiments of the present invention. It is preferred that the amount of coal extract added to the petroleum pitch prior to the thermal processing of the petroleum pitch be about 10-50 weight percent and about 50 to 90 weight percent petroleum pitch in the total feedstock although larger percentages of coal extract up to about 5-95 percent can be employed, if desired.

It will be appreciated that the present invention has provided a method of creating a unique, high-compressive strength, coal-derived carbon foam material, which may be graphitized, and also possesses a great number of desirable properties. An alternate approach employs petroleum feedstock or a combination of petroleum pitch and coal feedstock.

All of this is accomplished by starting with bituminous coal or petroleum feedstock or a combination of both and employing either the hydrogenated anisotropic approach or the solvent approach without prior hydrogenation to produce an isotropic structure or a blend of the two materials to produce the desired level of anisotropy. In addition, the void or bubble size and density of the carbon foam may be controlled by adjusting the volatile content of the coal-derived pitch precursor or asphaltene which is to be coked and/or adjusting the ballast pressure which is applied externally. This void or bulk size is controlled without requiring dependence on an external blowing/foaming agents. The solvent separation of step 10 of Figure 1 and step 30 of Figure 2 serve to remove inorganic species and/or also to select the proper fraction to make the desired foam.

The process of producing a foam depends primarily on two features: (a) the presence of volatile material which, in the preferred practice of the invention, will be internally present; and (b) the viscosity of the parent pitch may be altered by cross-linking which results from devolatilization or the presence of an externally-added cross-linking agent. If desired, for example, a plasticizer may be employed to adjust the viscosity to the desired value. At high viscosity, pitch flow is restricted and this resists the coalescence of bubbles produced by devolatilization. This results in a high-density

foam with small bubble size. At lower viscosity, bubbles can coalesce and a more open foam structure with larger bubbles is produced. The devolatilization is controlled by application of external pressure from a ballast tank, such as 16, 33 or 49. At high pressure, less movement of the bubbles takes place and, as a result, the foams are more dense. At low external pressure, the bubbles tend to coalesce and flow so a less-dense foam is produced.

Whereas particular embodiments of the invention have been described herein for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details may be made without departing from the invention as set forth in the appended claims.

We claim:

1. A method of making a carbon foam material with anisotropic domains comprising

creating a coke precursor by hydrogenating and de-ashing petroleum feedstock,

dissolving said hydrogenated petroleum feedstock having asphaltenes and oils in a solvent,

separating said asphaltenes from said oils, and

coking said asphaltenes by heating at a temperature of about 300°C to 500°C for about 6 minutes to 24 hours to devolatilize and foam said asphaltenes and cooling said carbon foam.

2. The method of claim 1 including

graphitizing said carbon foam at a temperature of at least 2600°C.

3. The method of claim 1 including

after coking but prior to graphitizing, calcining said carbon foam.

4. The method of claim 2 including

effecting said hydrogenation at a temperature of about 325°C to 450°C.

5. The method of claim 3 including

effecting said hydrogenation at a pressure of about 500 to 2500 psig hydrogen cold.

6. The method of claim 5 including

effecting said hydrogenation for a time of about 15 minutes to 1.5 hours.

7. The method of claim 2 including

effecting said coking of said asphaltenes at a rate of about 0.5°C to 2°C per minute until the desired coking temperature has been reached.

8. The method of claim 1 including

effecting said coking at pressure of about 50 to 1000 psig.

9. The method of claim 1 including
effecting said coking for a time of about 15 minutes to 5 hours.

10. The method of claim 1 including
controlling the degree of anisotropy at least in part by mixing asphaltenes from hydrogenated coal with asphaltenes from unhydrogenated coal prior to said coking.

11. The method of claim 10 including
employing about 10 to 50 weight percent coal pitch and about 50 to 90 weight percent petroleum pitch in the total feedstock.

12. The method of claim 1 including
creating said carbon foam with voids of generally uniform size.

13. The method of claim 12 including
controlling said void size at least in part by controlling the volatile content of said asphaltenes prior to coking.

14. The method of claim 12 including
controlling said void size at least in part by controlling the pressure applied during the coking step.

15. The method of claim 12 including
said controlling of said void size contributing to the compressive strength of said carbon foam.

16. The method of claim 1 including
prior to said hydrogenating and de-ashing, preheating said petroleum feedstock to about 300°C to 500° C to soften the same.

17. The method of claim 2 including
said graphitized foam with anisotropic domains having a compressive strength of greater than 600 lb/in^2.

18. The method of claim 12 including
producing an open-celled carbon foam material by said method.

19. The method of claim 1 including
after said hydrogenation but prior to said coking removing inorganic impurities from said asphaltenes by said separation.

20. The method of claim 10 including

employing as said coal, coal having a size of about -60 to -200 mesh.

21. The method of claim 2 including

effecting said graphitizing at a temperature of about 2600°C to 3200°C.

22. The method of claim 21 including

effecting said calcining at about 975°C to 1025°C.

23. The method of claim 20 including

creating said graphitized foams with a density of about 0.2 to 2 g/cc.

24. The method of claim 9 including

effecting said mixing of said asphaltenes in a solvent,

evaporating said solvents, and

subsequently effecting said coking.

25. The method of claim 17 including

impregnating said open-celled carbon foam material with pitch.

26. The method of claim 23 including

graphitizing said pitch impregnating said carbon foam.

27. The method of claim 2 including

prior to said separating said asphaltenes from said oils removing inorganic matter from said solvent.

28. The method of claim 27 including

employing tetrahydrofuran as said solvent.

29. The method of claim 28 including

effecting said separation of said asphaltenes from said oils by employing toluene.

30. The method of claim 1 including

evolving low molecular weight volatiles from said petroleum stock and effecting cross-linking of said petroleum stock during said coking stage.

about room temperature.

31. The method of claim 16 including

evolving low molecular weight volatiles from said petroleum stock and effecting cross-linking of said petroleum stock during said preheating stage.

32. The method of claim 16 including

effecting said preheating from about 0.1 to 24 hours.

33. The method of claim 16 including

subsequent to said preheating, cooling said petroleum pitch to about room temperature.

34. The method of claim 33 including

subsequent to said cooling converting said petroleum pitch to a powder.

35. The method of claim 1 including

prior to said hydrogenating and de-ashing admixing said petroleum feedstock with bituminous coal feedstock.

36. The method of claim 35 including

effecting said mixture of said bituminous coal feedstock and said petroleum feedstock with said coal feedstock being about 10-50 percent by weight and the petroleum feedstock being about 50 to 90 percent by weight of the total feedstock.

37. A method of making an isotropic carbon foam material comprising

creating a coke precursor by admixing petroleum feedstock and coal feedstock,

dissolving said admixed feedstock having asphaltenes and oils in a solvent,

separating said asphaltenes from said oils, and

coking said asphaltenes by heating at a temperature of about 300°C to 500°C for about 6 minutes to 24 hours to devolatilize and foam said asphaltenes and cooling said carbon foam.

38. The method of claim 37 including

graphitizing said carbon foam at a temperature of at least 2600°C.

39. The method of claim 38 including

after coking but prior to graphitizing, calcining said carbon foam.

40. The method of claim 38 including

employing about 10 to 50 weight percent of said coal feedstock and about 90 to 50 weight percent of said petroleum feedstock.

41. The method of claim 40 including

effecting said solvent separation in an inert gas environment.

42. The method of claim 38 including

subsequent to said preheating, cooling said petroleum pitch to about room temperature.

43. The method of claim 41 including

effecting said solvent separation without prior hydrogenation of said bituminous coal.

44. The method of claim 39 including

effecting said coking at pressure of about 50 to 1000 psig.

45. The method of claim 39 including

effecting said coking for a time of about 15 minutes to 5 hours.

46. The method of claim 45 including

creating a carbon foam having voids of generally uniform size.

47. The method of claim 45 including

controlling said void size at least in part by controlling the volatile content of said asphaltenes prior to coking.

48. The method of claim 47 including

controlling the carbon void size at least in part by controlling the pressure applied during the coking step.

49. The method of claim 40 including

creating said isotropic graphitized carbon foam to have a compressive strength of greater than 600 lb/in^2.

50. The method of claim 37 including

producing an open-celled carbon foam material by said method.

51. The method of claim 39 including

effecting removal of inorganic impurities by said separation.

52. The method of claim 33 including

prior to said separating of said asphaltenes from said oils removing inorganic matter from said solvent.

53. The method of claim 52 including

employing tetrahydrofuran as said solvent.

54. The method of claim 50 including

effecting said separation of said asphaltenes from said oils by employing toluene.

55. The method of claim 54 including

effecting said calcining at about 975 °C to 1025 °C.

56. The method of claim 37 including

evolving low molecular weight volatiles from said feedstock and effecting cross-linking of said petroleum stock during said coking.

57. The method of claim 56 including

effecting said cooling of said carbon foam to about room temperature.

58. The method of claim 57 including

subsequent to said cooling converting said petroleum pitch to a powder.

59. The method of claim 37 including

employing bituminous coal as said coal feedstock.

60. A petroleum feedstock derived carbon foam comprising

a body portion having a plurality of voids of generally uniform size therein and said body having anisotropy domains.

61. The carbon foam material of claim 60 including

said carbon foam being graphitized carbon foam.

62. The carbon foam material of claim 61 including

said graphitized carbon foam having a compressive strength greater than about 600 lb/in^2.

63. The carbon foam material of claim 60 including

said carbon foam material has at least a major portion of voids in communication with the exterior thereof filled with a pitch material.

64. The carbon foam material of claim 63 wherein said pitch material contained within said voids is graphitized.

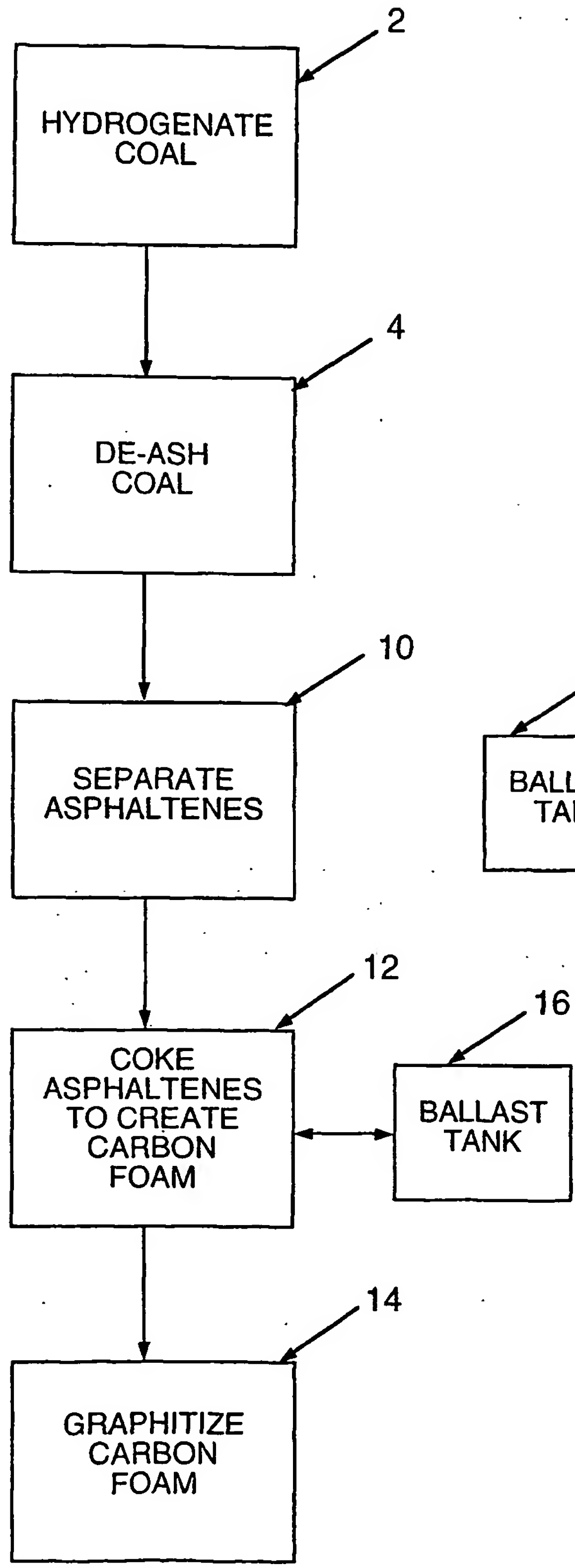
2
HYDROGENATE COAL
4
DE-ASH COAL
10
SEPARATE ASPHALTENES
12
COKE ASPHALTENES TO CREATE CARBON FOAM
16
BALLAST TANK
14
GRAPHITIZE CARBON FOAM

FIG. 1

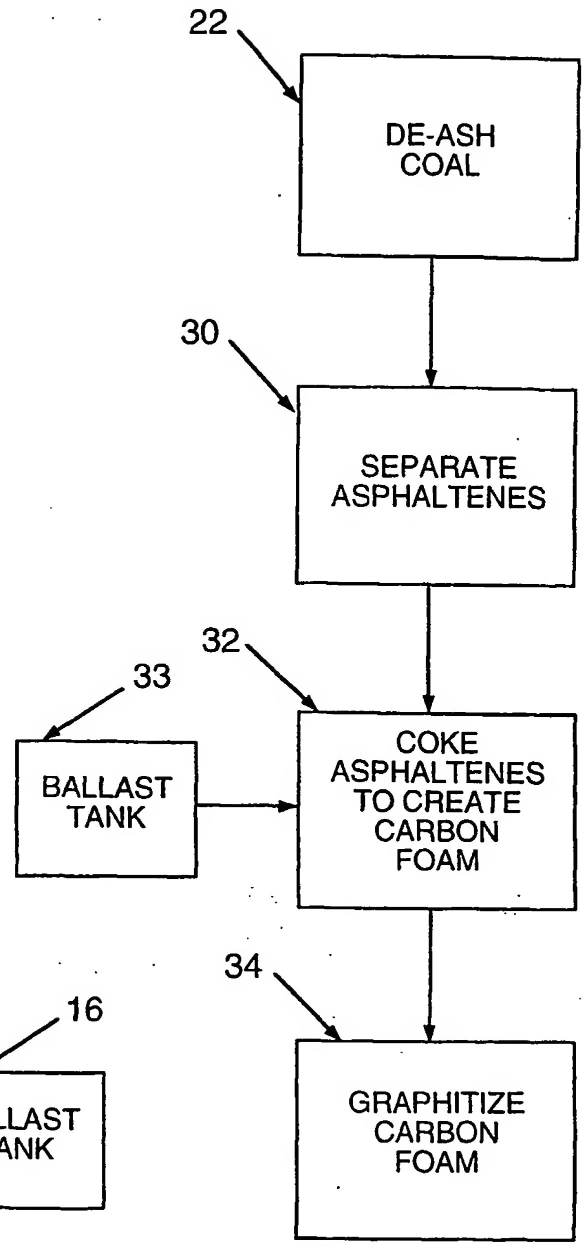
22
DE-ASH COAL
30
SEPARATE ASPHALTENES
32
33
BALLAST TANK
COKE ASPHALTENES TO CREATE CARBON FOAM
34
GRAPHITIZE CARBON FOAM

FIG. 2

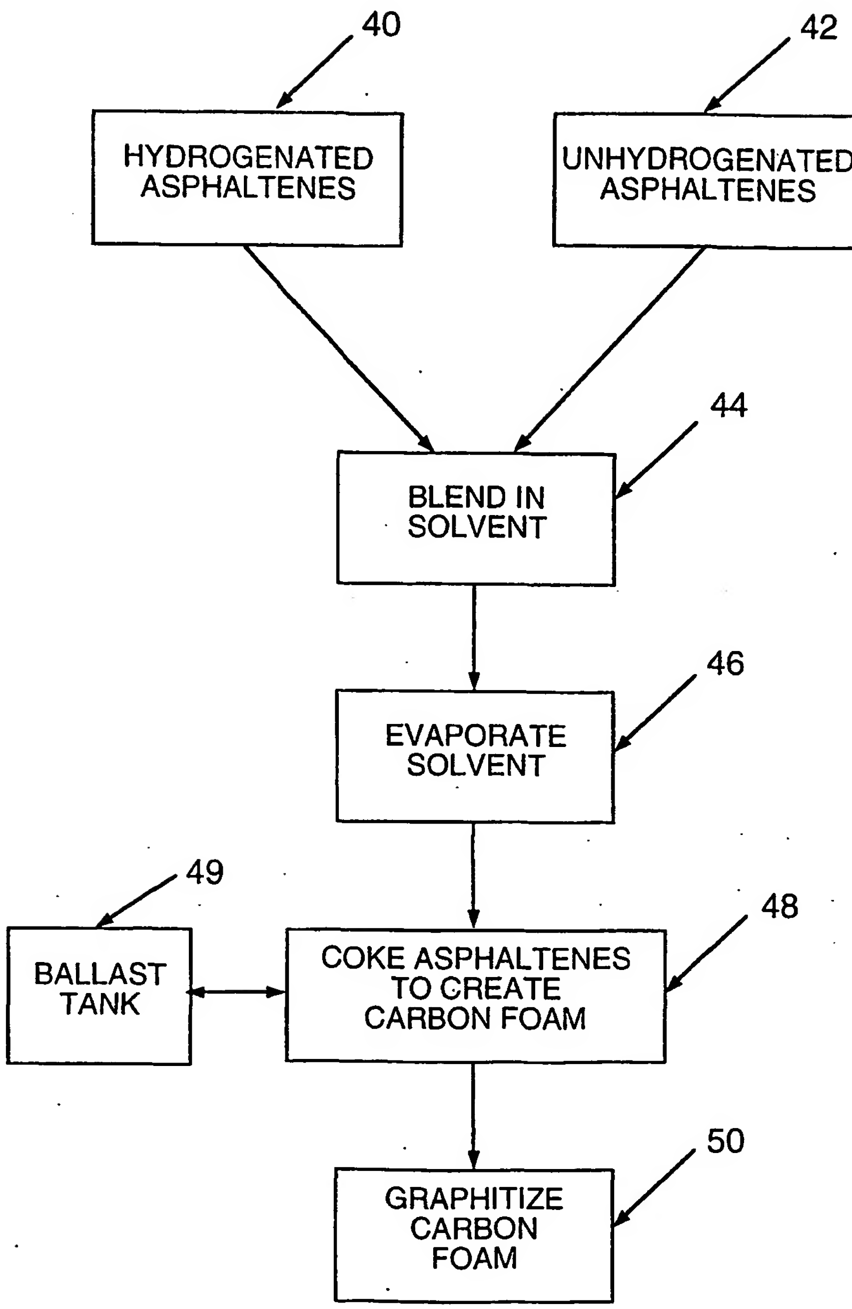
40
42
HYDROGENATED ASPHALTENES
UNHYDROGENATED ASPHALTENES
44
BLEND IN SOLVENT
46
EVAPORATE SOLVENT
49
48
BALLAST TANK
COKE ASPHALTENES TO CREATE CARBON FOAM
50
GRAPHITIZE CARBON FOAM

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/26269

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 31/02
US CL : 423/445R, 448
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/445R, 448

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,961,814 A (KEARNS) 05 October 1999, column 3.	60-64

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 NOVEMBER 2001	13 DEC 2001

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